Disintegration of network structure of bismaleimide–triazine resin by electron beam irradiation

Tsuneo Sasuga and Miyuki Hagiwara
Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Gunma 370–12, Japan

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The effect of electron beam irradiation on highly crosslinked bismaleimide–triazine resin (BT resin) was studied by measuring tensile properties and mechanical relaxation behaviour. Tensile strength and elongation at room temperature did not show any marked change up to 50 MGy. On the other hand, the peak temperature of β relaxation ($\sim 280^\circ$C), which is closely involved with the glass transition, tended to shift lower with increasing dose. Number-average molecular weight between crosslinking points, M_c, was calculated from the shift of the glass transition temperature and the shear modulus at the rubbery plateau. The proportion of crosslink points disintegrated under irradiation was estimated from the change in M_c as follows: 8% at 10 MGy, 22% at 20 MGy, 32% at 30 MGy and 60% at 50 MGy irradiation. From the change in profile of the γ relaxation peak ($\sim -100^\circ$C), it is estimated that the disintegration takes place in bis(phenol-A) moiety.

(Keywords: bismaleimide triazine resin; electron beam; deterioration; tensile properties; viscoelastic properties; disintegration; network structure)

INTRODUCTION

Radiation effects on fibre-reinforced plastics (FRP) that consist of a highly crosslinked polymer matrix, such as epoxy resin, have been reported[1–12]. The radiation resistance of FRP is relevant for their use as insulation for superconducting magnets for a magnetically confined fusion reactor. Several factors can be considered in the deterioration of FRP, e.g. damage to the matrix resin, the fibre itself, and the resin–fibre interface. In most studies, however, radiation deterioration of FRP was evaluated by measuring mechanical strength of bulk FRP. To understand the mechanism of deterioration of composite materials, knowledge of damage to each component is required.

Generally, the matrix resin used in FRP has high degree of crosslinking. For example, molecular weight between crosslink points (M_c) is about several hundreds for FRP matrix resin. On the other hand, M_c of ordinary elastomers is $\sim 10^4$. Because of the high degree of crosslinking, the ultimate elongation of highly crosslinked matrix resin is very small and its value is less than 10%. Therefore, a tensile test, which is usually used for evaluation of radiation damage of elastic polymers, may not be adequate for such matrix materials. Another quantitative measure, for example, change in the number of crosslink points, would be necessary to evaluate radiation damage in highly crosslinked materials.

Murayama *et al.*[13] deduced average molecular weights between crosslink points in epoxy resins with different crosslinking densities, using the change in glass transition temperatures (T_g) and shear modulus above T_g obtained by dynamic mechanical measurement. This method would be useful for estimating the radiation-induced disintegration of network structure in crosslinked materials.

Recently bismaleimide–triazine (BT resin) has been developed as a matrix polymer in FRP for high temperature use. Cured BT resin consists of aromatic imide rings, triazine rings, triazine-imidazole rings, and bis(phenol A) groups. Our work on radiation damage of several aromatic polymers[14] predicts that these groups are resistant against radiation, except bis(phenol A). BT resin can be considered a useful matrix resin for use in radiation fields.

In this paper, a mechanical relaxation method study has been made of the radiation damage of BT resin. The degree of radiation-induced disintegration of the network was evaluated and the radiation susceptibility of component chemical structures is discussed.

EXPERIMENTAL

Cured BT resins, BT-2100 and BT-3109, were kindly supplied from Mitsubishi Gass Kagaku Co. Ltd. BT-2100 consists of only bismaleimide and triazin monomers, while BT-3109 contains a small amount of a third component. Average molecular weight of the resins before curing is about 300. Curing was carried out in three steps: at 150°C for 2 h, 180°C for 2 h, then 240°C for 2 h. Strips measuring 100 × 5 × 0.5 mm were irradiated in an electron beam at a dose rate of 5×10^3 Gy s^{-1} (acceleration voltage = 2 MeV, current = 1.5 mA) on a stainless steel plate with water cooling jacket.

The tensile test was carried out on strips attached to tabs on both sides at a crosshead speed of 10 mm min^{-1} at 25°C. The length between tabs was 30 mm. The

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elongation at break was obtained by dividing the deformation length by the length between the tabs (30 mm) and Young's modulus was obtained from the initial stress–deformation relationship. Data points are represented by average value with standard deviation on seven to ten specimens.

The dynamic mechanical relaxation was measured on strips of BT-2100 with the specimen size described above with a torsion pendulum type apparatus (Rhesca RD 1100) with frequency of 0.2 to 1 Hz in the temperature range of −160°C to 350°C.

RESULTS

Tensile strength, Young's modulus, and ultimate elongation as a function of dose are shown in *Figure 1* for BT-2100 and in *Figure 2* for BT-3109. Although data are scattered over a relatively wide range, the tensile strength and the elongation seem to decrease with increasing dose, and Young's modulus seems to increase above 30 MGy.

Figure 3 shows temperature dependence of dynamic shear modulus (G') and the mechanical loss factor (logarithmic decrement) of unirradiated BT-2100. Two discrete relaxation peaks were observed at −100°C (γ) and at 285°C (β). The β relaxation peak can be attributed to molecular motion in the transition from the glassy to the elastic state because it accompanies a rapid decrease in shear modulus. The γ relaxation is due to local motion of various chemical groups in the polymer chain, but the detailed assignment is not clear.

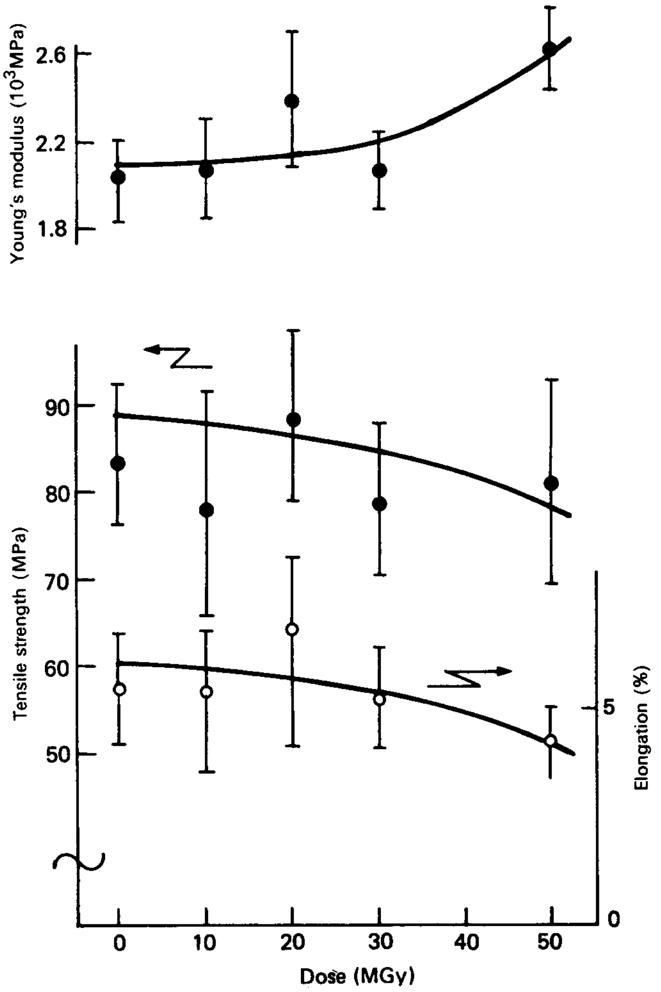

Figure 1 Tensile properties of BT-2100 as a function of dose

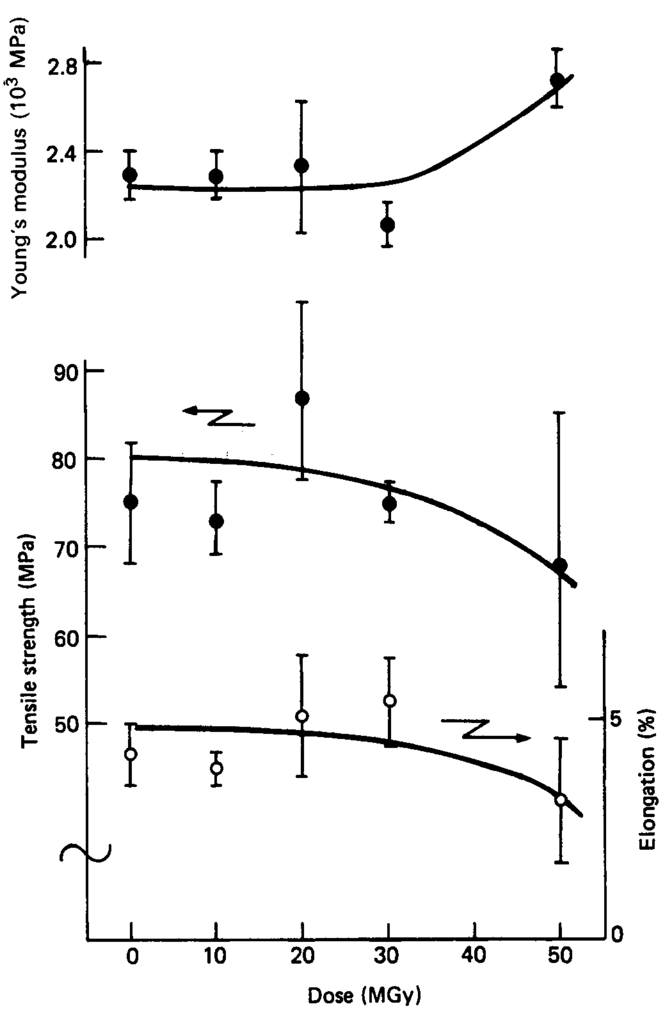

Figure 2 Tensile properties of BT-3109 as a function of dose

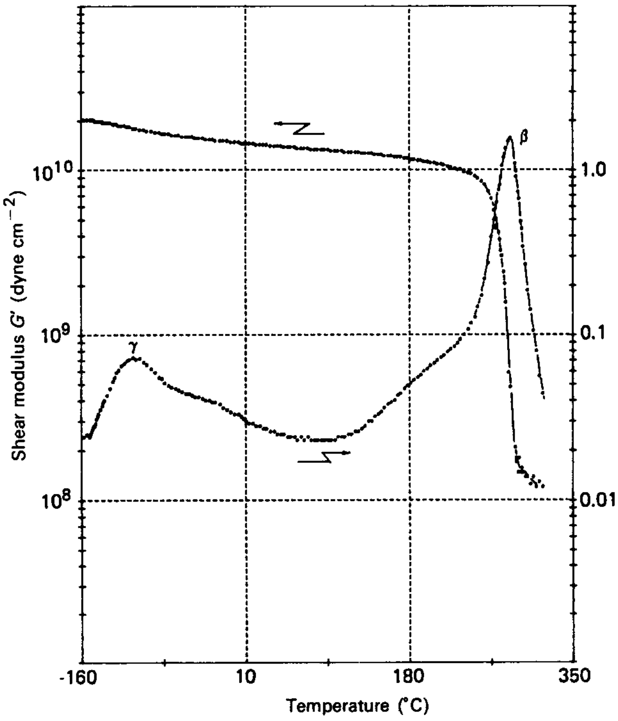

Figure 3 Mechanical relaxation spectra of unirradiated BT-2100

In *Figure 4* temperature dependence of mechanical losses between unirradiated specimens and those irradiated with 20 MGy is compared. No substantial difference is observed in the γ relaxation region except

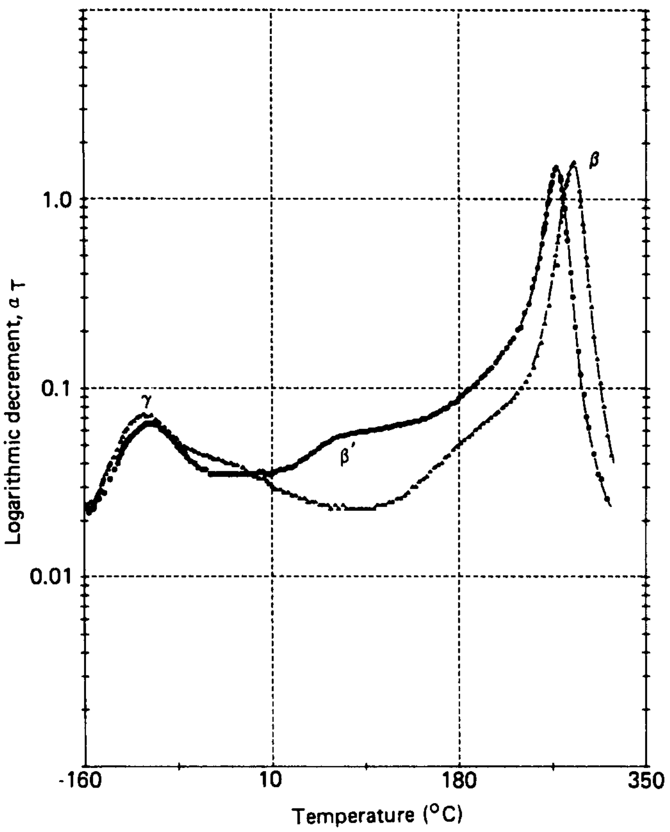

Figure 4 Mechanical loss of unirradiated (▲) and 20 MGy-irradiated BT-2100 (●)

that the profile is slightly affected in the temperature range of −70 to 0°C, but from 20°C to *ca.* 150°C a broad peak appears in the irradiated specimen and the β relaxation peak shifts to lower temperature. The broad peak ranging from 20 to 150°C is the β′ relaxation.

Figure 5 shows the loss *versus* temperature curves of the first and second runs of the 20 MGy-irradiated specimen. In the second run, the γ peak profile reforms to that of the non-irradiated specimen and the β′ relaxation peak disappears. Further, the β relaxation peak shifts to a lower temperature and broadens.

Figure 6 shows the temperature dependence of the shear modulus of specimens irradiated with various doses. The temperature at which a sharp decrease of the modulus occurs tends to fall with increasing dose, indicating that the glass transition temperature decreases with dose. The shear modulus above T_g (rubbery plateau) is the order of 10^8 dyne cm^{-2} and the value decreases with increasing dose. It decreases to the order of 10^7 dyne cm^{-2} by irradiation up to 50 MGy.

DISCUSSION

As shown in *Figures 1* and *2*, the changes in the tensile strength and elongation are very small, but the two tensile parameters tend to decrease in parallel with increasing dose. Large decrease in elongation with increasing dose is often observed in non-crosslinked elastic polymers. This is interpreted qualitatively as chain scission and/or crosslinking. As mentioned in the Introduction, the ultimate elongation of highly crosslinked materials is very small, so that any change below the glass transition temperature may not be clearly observed, even if further crosslinking and/or disintegration of the network take place. To understand radiation effects of highly crosslinked materials direct knowledge about change in molecular weight between crosslink points, M_c, may be useful.

The results in *Figures 4* and *6* show clearly that the glass transition temperature decreases with increasing dose.

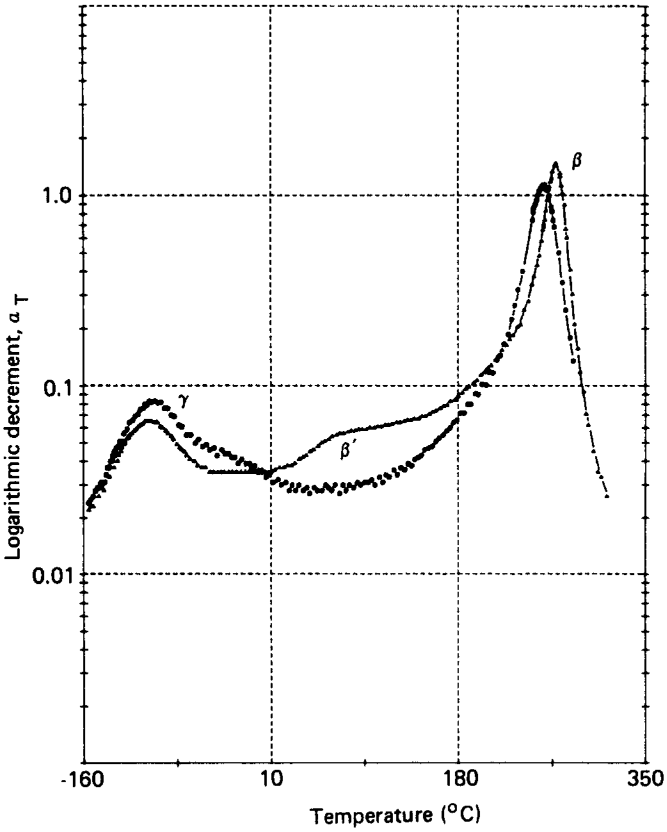

Figure 5 Mechanical loss of 20 MGy-irradiated BT-2100: (▲), first run; (●), second run

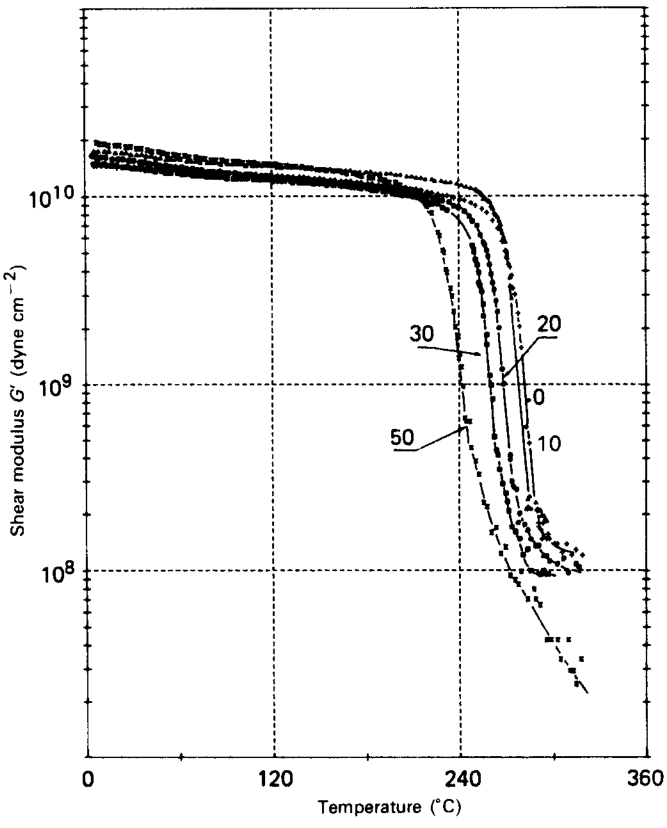

Figure 6 Temperature dependence of shear modulus for various irradiation doses: +, unirradiated; ▲, 10 MGy; ○, 20 MGy; □, 30 MGy; ×, 50 MGy

The relation between the change in glass transition temperature T_g and number-average molecular weight of network chain, M_c, has been reported by many authors[15-21]. Nielsen[18] presented a simple method to estimate M_c from the change in the glass transition temperature:

$$M_c = 3.9 \times 10^4/(T_g - T_{g_0}) \qquad (1)$$

where T_{g_0} is the glass transition temperature of non-crosslinked polymer. As direct measurement of T_{g_0} of BT resin is impossible, it was estimated by equation (2), derived by Tobolsky *et al.*[21]:

$$G' = \rho(r_i^2/r_f^2)RT/M_c\{1-(2M_c/M_n)\} \qquad (2)$$

where r_i^2/r_f^2 is the ratio of the mean square end to end distance of polymer chain in the sample in solid state to the distance in a randomly coiled chain (in solution), ρ is density, R is the gas constant, T is the absolute temperature, and M_n is the molecular weight of the backbone chain. It is rather difficult to determine the ratio of r_i^2/r_f^2 for BT resin. If it is assumed that in the solid state the polymer chains exist in random coil conformation, the ratio becomes equal to 1.0. The term $\{1-(2M_c/M_n)\}$ is a correction for chain ends. Since $M_c \gg M_n$ in highly crosslinked polymers this term also is equal to 1.0.

Based on the above assumptions, equation (2) can be simplified to:

$$G' = \rho RT/M_c \qquad (3)$$

The shear modulus of unirradiated BT 2100 in the rubbery plateau region is 1.21×10^8 dyn cm^{-2} at 592 K. Hence M_c can be estimated to be 505 from equation (3) and then T_{g_0} to be 208°C from equation (1). The change in M_c by irradiation can be calculated by introducing $T_{g_0} = 208$°C and T_g of irradiated polymers into equation (1). T_g can be measured by mechanical relaxation. Results are listed in *Table 1*, in which density of crosslink point ν_e was calculated from the relation $\nu_e = \rho/M_c$ (mol cm^{-3}).

M_c of unirradiated polymer is thought to be reasonable, in comparison with the molecular weight of raw BT resin (300). The increase in M_c and decrease in ν_e by irradiation shows occurrence of radiation-induced disintegration of the network structure. From the data, about 8% of original network chains are disintegrated by 10 MGy irradiation. With further irradiation, the amount of disintegrated chains as follows: 23% by 20 MGy, 32% by 30 MGy and 58% by 50 MGy.

To obtain M_c and ν_e, some assumptions are made; there are no experimental grounds for assuming that $r_i^2/r_f^2 = 1$, so that the obtained M_c and ν_e are relative values. However, the values obtained by this method explain well mechanisms of highly crosslinked materials by irradiation.

In spite of rather large disintegration of network structure with increasing dose, the tensile properties do not change markedly up to 30 MGy. It is considered that the elongation is scarcely affected by partial disintegration of crosslinking, because the elongation of highly crosslinked polymer is restricted by the remaining network structure. For irradiation > 30 MGy, elongation and tensile strength decrease simultaneously and Young's modulus increases with increasing dose. This shows that the polymer becomes increasingly stiff and brittle. This deterioration of mechanical properties may be caused by an excessive disintegration of the network.

As described before, irradiation introduced a new mechanical relaxation occurring at temperatures extending from 20°C to just below the glass transition temperature (*Figure 4*; β' relaxation). The same irradiation effects were observed in polymers such as polysulphone[22], polyacrylate[23] and polyether-ether-ketone[24]. The magnitude of loss of the β' relaxation was decreased by heat treatment under T_g and disappeared after treatment above T_g. A similar kind of relaxation appears in unirradiated specimens obtained by high speed quenching from temperatures above T_g, which suggests that the β' relaxation is due to the rearrangement of polymer chains in a quasi-stable state such with loosened packing caused by high speed quenching. Since the β' relaxation of irradiated BT resin also disappears in the second run after heating above T_g (*Figure 5*), the radiation seems to give the same effect as the high speed quenching. Chain packing may be loosened by chain scission under irradiation.

The β relaxation peak in the second run of the 20 MGy-irradiated specimen shifts to a lower temperature and becomes broader than the one in the first run (*Figure 5*). Probably, disintegration proceeds during heating in the first run. The γ relaxation peak temperature is scarcely affected by irradiation, but the peak profile slightly changes, i.e. the loss factor in the range of −70 to 0°C decreases slightly (*Figure 4*). In the second run, the γ peak profile resembles closely the one of the unirradiated specimen (*Figure 5*). These results indicate that a moiety with an inherent conformation (chain packing) is selectively disintegrated and the original conformation reappears as a result of active molecular motion during the temperature rise through T_g in the first run. Detailed discussion of the chemical unit destroyed by irradiation is difficult because BT resin consists of many types of units. However, bis(phenol-A) group may be damaged rather selectively, because the local motion of polymers containing the bis(phenol-A) group appears at relatively high temperatures (*ca.* −50 to 0°C) and this group is relatively sensitive to radiation[14].

Finally, the radiation damage of highly crosslinked BT resin has very little effect on tensile parameters at room temperature although the disintegration of network structures proceeds markedly with increasing dose.

Table 1 Number-average molecular weight of network chain, M_c, and number of crosslinking points, ν_e

Dose (MGy)	0	10	20	30	50
T_g (°C)	285	279	269	261	241
M_c	505	549	639	736	1182
ν_e (mol cm^{-3})	2.5×10^{-3}	2.3×10^{-3}	1.9×10^{-3}	1.7×10^{-3}	1.0×10^{-3}

Disintegration of the network may markedly affect mechanical properties at low or high temperature rather than at room temperature and the properties at high strain speed such as in an impact test.

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